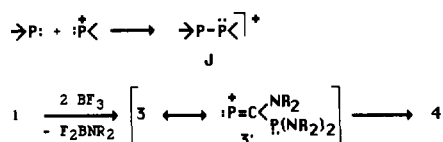
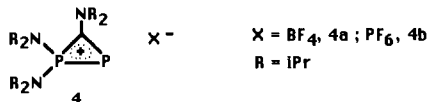


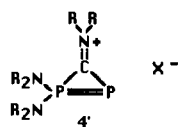
Scheme II



shift of the σ^1 -phosphorus, it is quite likely that the σ^3 -phosphorus atom should appear at much higher frequency and that the PP coupling constant should be smaller. In contrast, the high-field ^{31}P chemical shift^{2a} and the large J_{PP} were in favor of the diphosphirenium structure 4. The ^{13}C signal for the quaternary carbon appearing at 185.9 as a doublet, coupled only with the σ^2 -P ($J_{\text{PC}} = 81.2$ Hz), confirmed this hypothesis, since it has been shown that in phosphirenes the $^1J_{\text{PC}}$ coupling constant drastically decreases when the phosphorus coordination number increases.^{2a}



The structure of 4a has been clearly established by a single X-ray diffraction study.⁸ The thermal ellipsoid diagram of the molecule is shown in Figure 1, as well as the pertinent metric parameters. Several aspects of the structure merit discussion. No interaction with the tetrafluoroborate is observed, demonstrating the ionic character of 4a. The P1-P2 distance (2.095 (1) Å) is the range expected for a phosphinylidene- σ^4 -phosphorane ($-\text{P}=\text{P}^{\oplus}$);⁹ the P1-C1 (1.747 (4) Å) and P2-C1 (1.737 (4) Å) bond lengths are quite similar, and the C1-N2 distance (1.322 (4) Å) is comparable to that found in the tris(dimethylamino)cyclopropenium ion.¹⁰ These results as a whole and the fact that the geometry at both C1 and N2 is planar indicate a substantial participation of resonance structure 4'. This resonance form also explains the non-equivalence of the diisopropyl groups at the nitrogen bonded to the ring carbon, observed by NMR.



Since it is well-known that dicoordinated phosphirenium cations react with phosphanes to give the corresponding adduct J,¹¹ it seems reasonable to postulate the transient formation of the σ^1, σ^3 -diphosphaallenic cation 3 to rationalize the formation of 4. Indeed, compound 4 can be regarded as resulting from the intramolecular interaction of a monocoordinated phosphorus cation with a phosphane (Scheme II).

From these results the question arises of the relative stability of 1,3-diphosphaallenic cations and of the corresponding diphosphirenium cations, depending on the coordination of both

(8) Crystal data for 4a: $\text{C}_{19}\text{H}_{42}\text{BN}_2\text{F}_4\text{P}_2$, mol wt = 461.3, monoclinic, $P2_1/c$, $a = 15.122$ (4) Å, $b = 18.422$ (5) Å, $c = 18.284$ (5) Å, $\beta = 95.14$ (2)°, $V = 5073$ Å³, $Z = 8$ (asymmetric unit contains two independent molecules of 4a which are identical within the experimental errors), $D(\text{calcd}) = 1.208$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å (graphite monochromator), $T = -100$ °C. A Philips PW1100/16 diffractometer, equipped with a locally-built low-temperature device, was used to collect 5885 reflections ($3^\circ < 2\theta < 51^\circ$) on a yellow crystal $0.20 \times 0.20 \times 0.28$ mm. Of these, 4357 were observed [$I > 3\sigma(I)$]. Empirical absorption corrections and Lorentz and polarization corrections were applied to the data. All non-hydrogen atoms were located by direct methods, and they were refined anisotropically. The hydrogen atoms were included as idealized contributions. $R = 0.046$, $R_w = 0.074$, GOF = 1.62, final residual = $0.28 \text{ e } \text{Å}^{-3}$. All computation used MOLEN on a VAX computer: Frenz, B. A. The Enraf-Nonius CAD4-SDP. In *Computing in Crystallography*: Schenk, H., Olthof-Hazekamp, R., Van Koningveld, H., Bassi, G. C., Eds.; Delft University Press, 1978; pp 64-71.

(9) Schoeller, W. W. In *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O. J., Eds.; Thieme: Stuttgart, 1990; p 24.

(10) Ku, A. T.; Sundaralingam, M. *J. Am. Chem. Soc.* 1972, 94, 1688.

(11) (a) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* 1976, 15, 3042. (b) Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* 1981, 20, 2916. (c) Schmidpeter, A.; Lochschmidt, W. S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 226.

phosphorus atoms. The only other relevant molecule is I which possesses a linear structure.⁴ We are currently investigating other $1\sigma^x, 3\sigma^y$ -diphosphaallenic cations.

Acknowledgment. Thanks are due to Dr. Grützmacher for valuable discussions and to CNRS for financial support of this work.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, bond distances, and angles and ORTEP plots of the two molecules of 4a (17 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

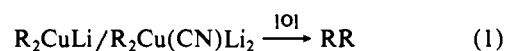
"Kinetic" Higher Order Cyanocuprates: Applications to Biaryl Synthesis

Bruce H. Lipshutz,* Konstantin Siegmann, and Emiliano Garcia

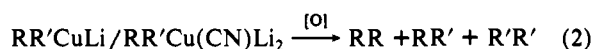
Department of Chemistry, University of California
Santa Barbara, California 93106

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A common side reaction associated with lithio organocuprates is their inadvertent oxidation leading to coupling between the ligands on copper (eq 1).^{1,2} With mixed-ligand reagents (i.e.,



$\text{R} \neq \text{R}'$, eq 2), statistical ratios of three products are usually produced,^{1c} rendering this carbon-carbon bond forming process in most circumstances synthetically unattractive.³



We now report that extremely high levels of unsymmetrical ligand couplings can be consistently achieved with diaryl higher order (HO) cuprates by controlling both temperature and mode of reagent formation, thereby resulting in a novel route to the biaryl nucleus.⁴

Combining *m*-anisyllithium (*m*-ArLi),⁵ *p*-anisyllithium (*p*-ArLi),⁵ and CuCN (1:1:1) in THF, cooling to -75 °C, and carrying out oxidation (with gaseous O₂)⁶ affords a 1:2:1 mix of biaryls. However, preformation of *m*-ArCu(CN)Li in 2-methyl tetrahydrofuran, cooling⁷ to -125 °C, and then introduction of *p*-ArLi followed by oxidation at this lowered temperature now leads to a 3.5:93:3.5 ratio favoring *m*-ArAr-*p*, Scheme I.⁸ Ex-

(1) (a) Lipshutz, B. H.; Sengupta, S. *Org. React. (N.Y.)* in press. (b) Posner, G. H. *Org. React. (N.Y.)* 1972, 19, 1. (c) Posner, G. H., *Org. React. (N.Y.)* 1975, 22, 253.

(2) (a) Cuprate oxidations forming C-C bonds have been utilized to enhance substrate/cuprate couplings,^{2b} to form symmetrical products,^{2c} and as a tool of analysis for distinguishing between HO and LO cuprates.^{2d} (b) Whitesides, G. M.; San Filippo, J.; Casey, C. P.; Panek, E. J. *J. Am. Chem. Soc.* 1967, 89, 5302. (c) Whitesides, G. M.; Fischer, W. F.; San Filippo, J.; Bashe, R. W.; House, H. O. *J. Am. Chem. Soc.* 1969, 91, 4871. (d) Bertz, S. H.; Gibson, C. P. *J. Am. Chem. Soc.* 1986, 108, 8286.

(3) For a few examples where unsymmetrical products have been successfully obtained from lithio cuprate oxidation, see ref 1c, Table IIc. For a review on autoxidations of Cu(I) complexes, see: Kaufmann, T. *Angew. Chem., Int. Ed. Engl.* 1974, 13, 291. See also: Camus, A.; Marsich, N. *J. Organomet. Chem.* 1972, 46, 385.

(4) Review: Bringmann, G.; Walter, R.; Weirich, R. *Angew. Chem., Int. Ed. Engl.* 1990, 29, 977.

(5) Schlosser, M.; Ladenberger, V. *J. Organomet. Chem.* 1967, 8, 193.

(6) Early experiments using *o*-dinitrobenzene or -toluene gave similar ratios; however, the yields and percent conversions were much lower.

(7) External, bath temperature.

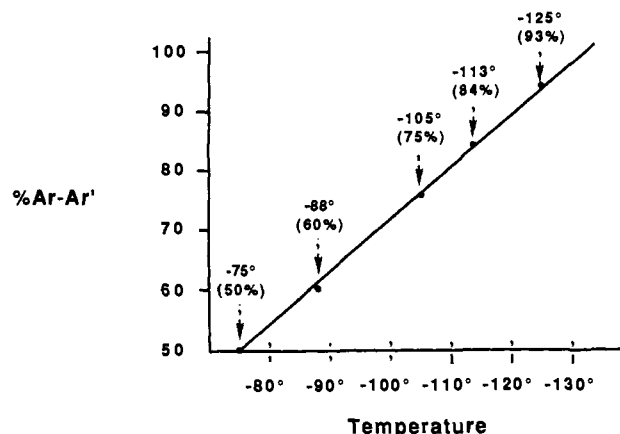


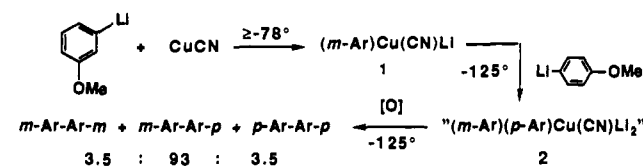
Figure 1.

Table I. Reactions of Kinetic Mixed Diarylcyanocuprates in 2-Methyltetrahydrofuran with O₂ at -125 °C

Aryllithiums		Biaryl product ^a	Yield(%) ^b	Ratio ^c
			(84%)	93 : 3.5 : 3.5
			(82%)	96 : 2 : 2
			(81%)	>98.5 : 1 : <0.5 ^d
			(84%)	96 : 2 : 2
			(83%)	96 : 1 : 1
			(90%)	>98 : <1 : <1
			(78%)	94 : 6 : 0 ^f

^aAll new products were fully characterized by spectroscopic means (IR, NMR, MS, and HRMS). ^bIsolated yield of unsymmetrical biaryl. ^cOf ArAr':ArAr':ArAr', as determined by capillary GC. ^dAmount of bi-*o*-anisyl observed. ^eVia metal/halogen exchange from the commercially available iodide. ^fNone of the dimer of (3-fluoro-4-methylphenyl)lithium was observed.

Scheme I



periments conducted at intermediate temperatures showed reduced selectivities for the percent unsymmetrical biaryl. When plotted (Figure 1), these values reveal an unexpected linear relationship! Reaction with preformed *p*-ArCu(CN)Li + *m*-ArLi gave identical

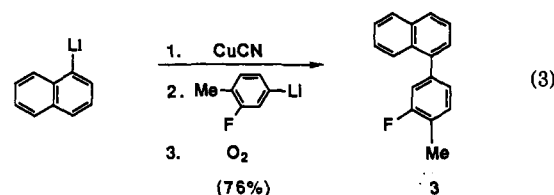
(8) As determined by capillary GC on a Hewlett-Packard 5890A instrument using a 60m fused silica J & W column. Authentic samples of symmetrical biaryls were prepared for comparison purposes.

results at -125 °C, establishing that either mode of ArLi addition to a lower order (LO) cyanocuprate 1 is acceptable.

Table I demonstrates the generality of this new method. Noteworthy features include the following: (1) the reactions are quite clean; (2) inexpensive molecular oxygen is employed, which simplifies workup and isolation; (3) hindered, ortho-substituted systems couple even when both aryl ligands are of this pattern; (4) electron-rich and -poor aryl rings participate, suggesting that stereoelectronic factors do not significantly influence the outcome; and (5) no special equipment is needed.⁹

Perhaps the most salient feature of this method is the implication that a "kinetic" cuprate can be generated under properly controlled conditions. Indeed, when the experiment in Scheme I was repeated with prior warming of 2 from -125 to -75 °C for a few minutes, recooling to -125 °C and then oxidation, a 1:2:1 mix of products was obtained. It is also rather timely¹⁰ to point out that attempts to reproduce these results with the LO analogue (*m*-Ar)(*p*-Ar)CuLi, prepared by substituting either Cu·LiI, Cu·LiBr, or Cu·LiPBu₃ in place of CuCN, led to uniformly inferior results (<40% yield) under otherwise strictly identical conditions.

Finally, our initial branching studies on this work have already shown promise (e.g. eq 3), and hence these and related couplings will be a subject of future reports from these laboratories.



Acknowledgment. Financial support provided by the National Science Foundation (CHE 90 05758), the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Swiss National Science Foundation (post-doctoral fellowship to K.S.) is gratefully acknowledged.

(9) A typical procedure for the preparation of 3 is as follows. An oven-dried 50-mL three-necked round-bottomed flask equipped with a T-top (for argon/vacuum), a thermometer adapter fitted with a gas dispersion tube (Aldrich, fritted-glass porosity 40–60μ), and a rubber septum was dried under vacuum with a Bunsen burner and then allowed to cool down to room temperature under argon, the process being repeated one additional time. Copper cyanide (90 mg, 1 mmol) was then added, and the flask was once again gently flame dried under vacuum and allowed to cool to room temperature under argon, to which was added 14 mL of dry 2-methyltetrahydrofuran. In another oven- and flame-dried 10-mL round-bottomed flask was added 6 mL of dry 2-methyltetrahydrofuran followed by 0.15 mL (1.0 mmol) of 1-iodonaphthalene. The flask was cooled to -78 °C, and 2.1 mmol of *t*-BuLi was added dropwise. After the addition, the reaction mixture was stirred at this temperature for 30 min. Identical treatment of 4-iodo-2-fluorotoluene (0.13 mL, 1.0 mmol) afforded the second aryllithium reagent. The flask containing the CuCN slurry was cooled to -78 °C, the precooled (-78 °C) naphthyl-lithium was added, and the mixture was allowed to warm to room temperature, forming a homogeneous solution. The resulting LO cyanocuprate was then recooled to -125 °C (pentane/N₂) and equilibrated at this temperature for ca. 10 min. The fluoroaryllithium reagent, cooled to -78 °C, was then added dropwise via cannula. After the addition was complete, the reaction mixture was stirred at -125 °C for another 10 min. TMEDA (0.7 mL) was then added dropwise, and the reaction mixture was stirred for another 10 min. The argon flow was then stopped, and dry O₂ (passed through a -78 °C trap) was bubbled through the reaction mixture, whereupon the solution turned dark after a few minutes. Oxygen flow was continued for 1 h, after which the reaction vessel was briefly evacuated and the argon flow reestablished. The reaction was then quenched with methanol/concentrated aqueous NaHSO₃ solution. The reaction mixture was allowed to warm to room temperature, acidified with concentrated HCl, and extracted (Et₂O), and the extracts were washed with brine. The organic phase was dried (Na₂SO₄) and filtered and the solvent removed under vacuum. Flash chromatography (silica gel) using hexanes/dichloromethane (9:1) afforded 0.1800 g (76%) of the desired product as a colorless oil.

(10) For a discussion on the existence of higher order cyanocuprates (e.g., 2), see: Bertz, S. H. *J. Am. Chem. Soc.* 1990, 112, 4031. Lipshutz, B. H.; Sharma, S.; Ellsworth, E. L. *J. Am. Chem. Soc.* 1990, 112, 4032. This work is but another example of the fundamental differences between HO cyano and LO cyanocuprates.